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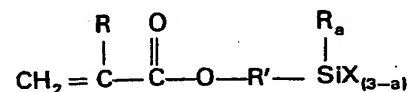
(54) **Silicone rubber compositions containing extending fillers and acryloxyalkylsilanes**

(57) The compositions comprise  
 (a) 100 parts by weight of a silicone rubber base comprising a polydiorganosiloxane in which the organic radicals are selected from methyl, vinyl, phenyl and 3,3,3-trifluoropropyl and a reinforcing silica filler and optionally an anti-crepe hardening agent;

(b) from 25 to 300 parts by weight of a siliceous extending filler;

(c) from 0.1 to 5 parts by weight of an organic peroxide vulcanizing agent; and

(d) from 0.08 to 0.3 part by weight of an acryloxyalkylsilane of the formula



wherein each R is hydrogen or methyl, R' is a C<sub>1-4</sub> alkylene radical, X is a C<sub>1-3</sub> alkoxy or an acetoxy radical, and a is 0 to 2. They may be press-cured without the need for post-curing.

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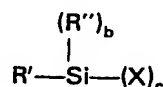
## SPECIFICATION

## Silicone rubber compositions containing extending fillers and acryloxyalkylsilanes

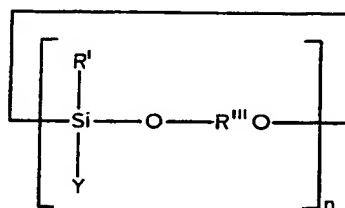
The present invention relates to silicone rubber compositions containing extending fillers and acryloxyalkylsilanes, to a method for their preparation and to cured elastomers prepared therefrom.

5 Elastomeric polydiorganosiloxane compositions are commercially available as fully compounded stocks and also as bases which are further compounded by the addition of materials such as catalysts, pigments and extending fillers. When extending fillers are added, the tensile strength of the cured composition is lowered, but part of the lost strength may be recovered by post-curing the composition.

10 U.S. Patent No. 3,341,489 discloses that if a certain olefinically unsaturated organosilicon material, such as vinyltriethoxysilane, is employed in minor amounts in an organopolysiloxane composition which is convertible to the cured, solid, elastic state, the resulting composition can be directly fabricated in to valuable elastomeric products without the necessity of an extended post-cure. The olefinically unsaturated organosilicon material is selected from a silane having the formula:



15 and a cyclic siloxane ester having the formula:



wherein R' is an olefinically unsaturated monovalent hydrocarbon radical, R'' is a hydrogen atom or a monovalent hydrocarbon radical which is free of olefinic unsaturation, R''' is a divalent aliphatic radical, X is an alkoxy, alkoxyalkoxy, alkoxyaryloxy or acyloxy radical or a halogen atom, Y is R'' or X, b is 0, 1 or 2, c is 1, 2 or 3, (the sum of b and c being equal to 3) and n is an integer having a value of from 1 to 10, preferably from 1 to 3 inclusive. The invention of this particular U.S. Patent is practised by forming a mixture of the polymer, filler and organosilanes, the order of addition not being critical.

There is no disclosure in the above-mentioned patent that an acryloxyalkylsilane will increase the tensile strength of a composition made with an extending filler such as ground silica and a silicone rubber base.

U.S. Patent No. 3,567,497 discloses the use of an acryloxyalkylsilane with a polymerizable vinyllic resin and a base member to produce a composite article of superior strength. It is disclosed that all siliceous materials including clay, diatomaceous earth and ground quartz are useful in the invention of this particular U.S. Patent. The vinyllic resins described as being of greatest interest are styrene, acrylic, methacrylic and polyester resins; and butadiene-styrene copolymers. The preferred method of use is to wet the surface of the base member with an aqueous solution of a hydrolysate of the defined silane and then allowing the surface to dry to yield a treated base member. It is disclosed that the treated materials of U.S. Patent No 3,567,497 can also be incorporated into natural polyolefinic rubber articles. Other types of rubbery materials which can be employed are organosiloxane rubbers which contain at least some silicon atoms to which are attached unsaturated aliphatic radicals.

Although the acryloxyalkylsilanes used in the present invention are disclosed in U.S. Patent No 3,567,497, this particular patent merely discloses the addition of such acryloxyalkylsilane to a vinyllic resin and thereafter applying the mixture to a base member or filler.

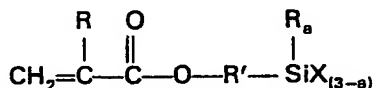
It is known that silanes containing vinyl and methacryl functionality may be used with mineral-filled peroxide cured elastomers including EPR, EPDM, silicone elastomers and crosslinkable polyethylene. It is broadly taught that the use of silanes at concentrations ranging from less than 0.5 parts by weight per hundred parts of filler to level above 2.0 parts by weight per hundred parts of filler improve the performance of relatively inexpensive extending fillers, including ground silica, calcined and hydrous clay, talc, wollastonite, alumina trihydrate, calcium carbonate and titanium dioxide.

The present invention relates to silicone rubber bases with extending fillers added to lower their cost. It has now been found that by adding certain acryloxyalkylsilanes to a silicone rubber base together with a siliceous extending filler, such as ground quartz or diatomaceous earth, the loss of tensile strength ordinarily caused by the addition of extending filler can be partially or completely overcome. This discovery allows the lowering of the cost of silicone rubber compositions without a loss of physical properties.

The use of an acryloxyalkylsilane in a silicone rubber composition which has been extended by the

addition of filler yields a cured product with optimum properties after being press-cured. It is not necessary to post-cure the product to obtain optimum properties.

Accordingly the present invention provides a composition comprising (a) 100 parts by weight of a silicone rubber base comprising a polydiorganosiloxane in which the organic radicals are selected from methyl, vinyl, phenyl and 3,3,3-trifluoropropyl and a reinforcing silica filler, and optionally an anti-crepe hardening agent, (b) from 25 to 300 parts by weight of a siliceous extending filler having an average particle size of less than 25 micrometres and a surface area of less than  $50 \text{ m}^2/\text{g}$ , (c) from 0.1 to 5 parts by weight of an organic peroxide vulcanizing agent capable of vulcanizing the silicone rubber base; and (d) from 0.08 to 0.3 part by weight of an acryloxyalkylsilane of the formula



wherein each R is a hydrogen atom or a methyl radical, R' is an alkylene radical having from 1 to 4 carbon atoms, X is an alkoxy radical having from 1 to 3 carbon atoms or an acetoxy radical, and a has a value of from 0 to 2.

In another aspect, the present invention provides a method of making a composition of the present invention which comprises mixing the above-identified components (a), (b), (c), and (d) until a homogeneous mixture is obtained.

The silicone rubber base used in the composition of the present invention can be any mixture of a polydiorganosiloxane and a reinforcing silica filler such as those of the types commercially available. The polydiorganosiloxane used in the present invention contains organic radicals selected from methyl, vinyl, phenyl and 3,3,3-trifluoropropyl, said radicals being bonded to the silicon atoms of the polydiorganosiloxane. The polydiorganosiloxanes are commonly of a viscosity of from 1000 Pa.s up to and including non-flowing gums. Such polydiorganosiloxanes are well known in the art and are commercially available.

A silicone rubber base contains a reinforcing silica filler to improve the physical strength of the polymer. Reinforcing silica fillers generally have a surface area of from 150 to greater than  $400 \text{ m}^2/\text{g}$ . Such reinforcing silica fillers are well known in the art and can be obtained commercially. The reinforcing filler used can be untreated, treated, or treated *in situ* during the manufacture of the silicone rubber base. The treated reinforcing silica fillers can be treated by any of the conventional methods described in the prior art, wherein the treating agents include organosilanes, organosiloxanes and silazanes. The amount of reinforcing filler can, for example, vary from 10 to as much as 100 parts by weight, with the usual amount varying between 15 to 75 parts by weight, per 100 parts by weight of the polydiorganosiloxane.

A silicone rubber base can also contain anti-crepe hardening agents which are used to reduce the reaction between the polydiorganosiloxane and the reinforcing silica which may cause the base to become harder or pseudo-vulcanized. Such a reaction can cause the base to become too "nervy" for further use.

Suitable anti-crepe hardening agents are well known in the art, and they can, for example, be such additives as hydroxyl endblocked short chain polydiethylsiloxane fluids. If the reinforcing filler is treated as discussed above, the silicone rubber base may not need an additional anti-crepe hardening agent.

The silicone rubber base may also contain minor amounts of additives to improve properties such as the heat stability, handling, compression set and oil resistance. A single silicone rubber base may be used or else a mixture of bases may be used to obtain the desired range of physical properties for the cured silicone rubber.

In use, a silicone base may be extended with an extending filler to increase the bulk of the composition. This helps to lower the cost of the finished part as the extending fillers are much lower in cost than the silicone rubber base. When a silicone rubber base is extended with an extending filler such as ground quartz, the tensile strength of the cured composition is much lower than that of the starting base. The amount of tensile strength lost depends not only upon the relative amounts of base and extending filler used but also upon the exact nature of both ingredients. If the mixture of silicone rubber base and extending filler is vulcanized and then given an oven post-cure, it is possible to restore a portion of the tensile strength loss due to the use of the extending filler, but the oven post-cure operation is a separate and costly additional process. In some cases, such as in insulating electrical wiring by an extrusion process, it is not practical to subject the cured product to an oven post-cure. It is a purpose of the present invention to eliminate a major portion of this tensile strength loss by the lowest cost means.

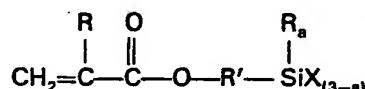
The siliceous extending fillers used in the present invention are finely ground particles of heat stable inorganic materials having an average particle size of under 25 micrometres. The finest extending fillers used approach a particle size and configuration such that they have a surface area of as high as  $50 \text{ m}^2/\text{g}$ . Examples of siliceous extending fillers useful in the present invention are ground quartz, diatomaceous earth and glass.

About 25 parts by weight of extending filler per 100 parts by weight of silicone rubber base is

necessary to significantly lower the cost of the composition. As much as 300 parts by weight of some extending fillers may be used where the lowest cost is necessary. A preferred level of extending filler, however, is from 25 to 200 parts by weight. The preferred siliceous extending fillers used in the present invention are ground quartz and diatomaceous earth with the most preferred filler being ground quartz having an average particle size of about 5 micrometres.

The compositions of the present invention contain an organic peroxide vulcanizing agent capable of vulcanizing the polydiorganosiloxane in the silicone rubber base. If the polydiorganosiloxane does not contain any vinyl radicals, it must be vulcanized with organic peroxides that are efficient in causing reactions in such polydiorganosiloxanes. Such organic peroxides are called "non-vinyl specific" and are represented by such organic peroxides as benzoylperoxide, dicumylperoxide and 2, 4-dichlorobenzoylperoxide. If the polydiorganosiloxane contains vinyl radicals, it can be vulcanized with either "non-vinyl specific" or "vinyl specific" organic peroxides. Representative of the "vinyl specific" organic peroxides are ditertiary-butylperoxide and 2,5-bis-(tert-butylperoxy)-2,5-dimethylhexane. All these organic peroxide vulcanizing agents and their properties are well known in the art and the properties of the cured silicone rubber can be altered by the type and amount of vulcanizing agent used to cure the composition. Typical changes due to such choices are well recognized in the art. The vulcanizing agent is present in an amount of from 0.1 to 5 parts by weight per 100 parts by weight of silicone rubber base, preferably of from 0.5 to 2.0 parts by weight.

The critical component of the compositions of the present invention is an acryloxyalkylsilane of the formula:



wherein each R is a hydrogen atom or a methyl radical, R' is an alkylene radical having from 1 to 4 carbon atoms, X is an alkoxy radical having from 1 to 3 carbon atoms or an acetoxy radical, and a has a value of from 0 to 2 inclusive. The silanes in which R is a methyl radical, a is 0, and X is a methoxy or acetoxy radical are preferred. The most preferred silane is gamma methacryloxypropyltrimethoxysilane because of its efficiency in restoring the tensile strength to a silicone rubber base that has been extended with a siliceous extending filler and also because of its commercial availability.

The acryloxyalkylsilanes used in the present invention are known in the art, and are disclosed in the aforementioned U.S. Patent No. 3,567,497.

As little as 0.08 parts by weight of silane per 100 parts by weight of silicone rubber base is enough to show a significant effect on the tensile strength of the cured composition.

Tests have indicated that at 0.5 parts by weight of the silane per 100 parts by weight of the silicone rubber base, the cured composition can adhere to aluminum plates used in the molding processes even though the plates have been coated with a release agent. For this reason, the practical upper limit for a composition used in a moulding process is 0.3 parts by weight of the silane per 100 parts by weight of the silicone rubber base. The most preferred level of silane depends on the nature of the other ingredients of the composition and also their amounts. The most preferred level may be determined easily by simple experimentation. The compositions of the present invention are prepared by any suitable means that will lead to a homogeneous mixture of the several components. Methods of mixing that are common in the silicone rubber art and which are suitable for the present invention include mixing with a dough mixer, a rubber compounding mill or with a Banbury mixer. The order of mixing is not critical. Ordinarily, however, the silicone rubber base is placed in the mixer, the extending filler and silane are added and mixed until homogeneous, and then the vulcanizing agent is added and mixing is continued until a homogeneous mixture is formed. Any additional additives such as heat stability additives, antioxidants, processing aids and pigments would ordinarily be added before the vulcanizing agent.

The curable homogeneous compositions of the present invention can be cured by any suitable means that will cause decomposition of the organic-peroxide vulcanizing agent, but heating is the preferred method. The time and temperature necessary to cause vulcanization of the compositions are dependent upon the organic peroxide vulcanizing agent chosen, the method of heating, the method of shaping the compositions to the desired configuration, and the thickness of the part. The temperature that is appropriate for a given set of conditions is well known in the silicone rubber art. Typical temperatures are from 110°C to 175°C for moulding operations to as high as 300°C for the ovens used in continuous hot air vulcanization operations.

Accordingly, the present invention also provides a process for the preparation of a cured silicone elastomer which comprises heating a composition of the present invention.

The compositions of the present invention can be shaped to the desired configuration by any of the well known methods of forming elastomeric curable compositions such as press molding, injection molding, calendaring, and extruding, both supported and unsupported.

When a silicone rubber base is extended with a low cost extending filler to lower the cost of the resulting overall composition, the tensile strength of the vulcanized silicone rubber is normally lower

than that of the unextended silicone rubber base. If the vulcanized rubber is subjected to an oven post-cure, it is possible to increase the tensile strength. Such a post-cure is commonly of from 1 to 24 hours duration at a temperature of from 150°C to 250°C and is an expensive step in the process of making silicone rubber parts. If the parts being made are formed by a continuous extrusion process such as for making tubing of insulated electrical wiring, the post-cure step becomes even more difficult and expensive. It was found that composition of the present invention had properties after a simple vulcanization step that were equivalent to those that were achieved only by post-curing if the silane was not present.

The compositions of the present invention are useful for making elastomeric articles suitable for uses customarily known for silicone rubber such as molded parts for high temperature applications, gaskets, O-rings, diaphragms, tubing and insulated electrical wiring. Equivalent products can be produced at a lower cost when compositions of the present invention are used.

The following Examples further illustrate the present invention. All parts are parts by weight.

#### EXAMPLE 1

A series of stocks was prepared and their physical properties were measured to illustrate the present invention.

(A) A commercially available silicone rubber designed for use in compounding general purpose silicone rubber stocks was used. The base was translucent with a specific gravity after molding of 1.09. The base consisted of a vinyl containing polydimethylsiloxane, a reinforcing fume silica, and a hydroxyl endblocked polydimethylsiloxane fluid to prevent crepe aging of the base.

The properties of the base after curing were determined by mixing 100 parts of the base with 1 part of organic peroxide vulcanizing agent to make a catalyzed base. The vulcanizing agent was 50 weight percent, 2,5-bis(tert-butylperoxy)-2,5-(dimethylhexane dispersed on an inert carrier powder. The catalyzed base was molded into a 1.9 mm. thick test slab, molding being carried out for 10 minutes at 170°C. in a press. The physical properties of the test slab were determined in accordance with the procedures described by ASTM-412 for tensile strength and elongation, by ASTM-D625, Die B for tear strength, and by ASTM—D2240 for durometer type A. The measured physical properties were as shown in Table 1 in which the tensile strength is recorded in megapascals (MPa) and the tear strength is recorded in kilonewtons per meter (KN/m).

(B) The test slab prepared as in (A) above was post-cured for 1 hour at 250°C in an air circulating oven. The physical properties were then measured to show the effect of post-curing the test slab. The properties were as shown in Table I.

(C) The silicone rubber base described in (A) above was compounded into a stock by mixing on a 2-roll mill, 100 parts by base, 100 parts of a ground quartz filler with an average particle size of 5 micrometres, and 1 part of the vulcanizing agent described in (A) above. The stock was then molded into test slabs following the procedure as described in (A) above and the physical properties measured as described above in (A). The properties were as shown in Table I.

A comparison of the tensile strength of (A) and (C) shows that the tensile strength of the vulcanized stock decreased when extending filler was added.

(D) The test slab prepared in accordance with the procedures described in (C) above was post-cured for 1 hour at 250°C. The physical properties were then measured to show the effect of post-curing test slabs containing an extending filler. The properties were as shown in Table I. The tensile strength was increased by post-curing.

(E) The preparation of the stock described in (C) above was repeated with the addition of 0.1 part of gamma-methacryloxypropyltrimethoxysilane to the other ingredients. The silane was added to the base on a 2-roll mill, then the extending filler and vulcanizing agent were added. The stock was then molded into test slabs as described in (A) above and the physical properties were measured following the procedures described in (A) above. The results were as shown in Table I.

A comparison of the results of (C) with (E) shows that the addition of the gamma-methacryloxypropyltrimethoxysilane increases the tensile strength of the vulcanized stock containing a large quantity of extending filler up to a value comparable to the tensile strength of the vulcanized base without the extending filler as shown by (A) above.

(F) The preparation of the stock of (E) above was repeated except that the amount of silane was increased to 0.2 part. The results were as shown in Table I.

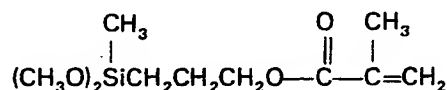
(G) The preparation of the stock of (E) above was repeated except that the amount of silane was increased to 0.5 part. The results were as shown in Table I. In order to obtain a good test slab at this level of silane, which is outside the scope of the present invention, it was necessary to use polytetrafluoroethylene film as a release agent during the press molding process.

#### EXAMPLE 2

A series of stocks was prepared using different silanes.

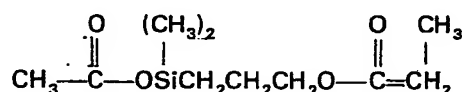
(J) A stock was prepared in accordance with the procedure of (E) above. This stock was then molded into test slabs as described in (A) above and the physical properties were measured as described in (A) above. The results were as shown in Table II.

(K) The stock described in (J) was prepared, but substituting 0.1 part of (gamma-methacryloxypropyl) methyldimethoxysilane



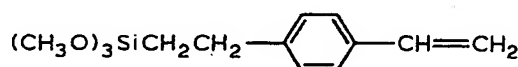
for the silane used in (J). The properties measured are recorded in Table II.

- 5 (L) The stock of (J) was prepared, but substituting 0.1 part of (gamma-methacryloxypropyl) dimethylacetoxysilane



for the silane used in (J). The properties measured are recorded in Table II.

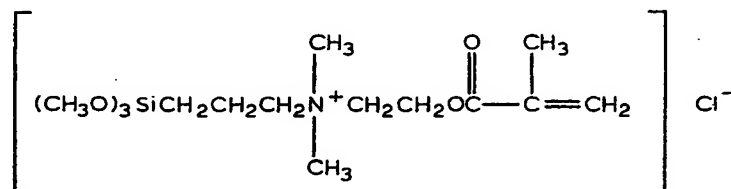
- 10 (M) The stock of (J) was prepared, but substituting 0.1 part of beta (vinylphenyl)ethyltrimethoxysilane.



for the silane used in (J). This silane, which is outside the scope of the present invention, was prepared by reacting divinylbenzene with trichlorosilane and then distilling the product. The beta (vinylphenyl) ethyltrichlorosilane is then methoxylated to yield the above trimethoxysilane. The properties measured

15 are recorded in Table II.

(N) The stock of (J) was prepared, but substituting 0.2 part of a solvent solution containing 50 weight percent of a reaction product of chloropropyltrimethoxysilane and dimethylaminoethylmethacrylate to yield a methacrylate functional silane of the formula



- 20 which is outside the scope of the present invention for the silane used in (J). The properties of the test slabs were measured and are recorded in Table II.

The acryloxyalkylsilanes used in the present invention were more efficient than other tested silanes. The tensile strength of a test slab had higher values when the silanes used in the present invention were added to the mixture of base, extending filler, and catalyst, as compared to other tested

25 silanes.

### EXAMPLE 3

Another series of stocks was made using different silanes to illustrate the superior efficiency of the present invention.

- 30 Each stock was compounded as described in Example 1(E) using 100 parts of the silicone rubber base used in (A) above 100 parts of ground quartz used in (C) above, 1 parts of vulcanizing agent used in (A) above and the amount and type of silane as shown in Table III.

Each stock was then molded into test slabs using the procedure described in Example 1 and the physical properties were measured as described in Example 1. The properties measured are recorded in Table III.

- 35 A comparison of the results of Table III shows that the silanes used in the present invention are more efficient than the silanes not covered by the present invention. The tensile strength of the test slabs containing the silane used in the present invention is higher than the tensile strength of the test slabs made using comparative silanes when each silane is used at the 0.1 part level.

### EXAMPLE 4

- 40 A series of stocks was made using different types of extending filler. The amount of filler used was that expected to produce a 50 to 60 durometer silicone rubber after vulcanizing.

(i) Stock was compounded consisting of 100 parts of the silicone rubber base described in (A) above, 0.1 part of gamma-methacryloxypropyltrimethoxysilane, 1 part of the vulcanizing used in (A) above and 100 parts of ground quartz.

The stock was molded, cured and tested as described in Example 1. The properties measured are recorded in Table IV.

(ii) The stock of (i) above was prepared but using 60 parts of diatomaceous earth instead of the ground quartz and 0.2 part of the silane instead of 0.1 part thereof.

5 The following samples were for comparative purposes:

(iii) The stock of (i) above was prepared using 100 parts of calcium carbonate instead of the ground quartz;

(iv) The stock of (iii) was prepared using a different calcium carbonate.

(v) The stock of (iv) was prepared using no silane;

10 (vi) The press-cured slab of (v) was oven-cured for 1 hour at 150°C and retested;

(vii) The stock of (i) was prepared using 50 parts of ground clay in place of the ground quartz;

(viii) The stock of (vii) was prepared using a different ground clay;

(ix) The stock of (iii) was prepared using no silane; and

(x) The press-cured slab of (ix) was oven-cured for 1 hour at 150°C and retested.

15 A comparison of the results in Table IV show that the quartz and diatomaceous earth extending fillers give the highest tensile strengths.

#### EXAMPLE 5

A series of samples was made to illustrate the use of a different type of organic peroxide vulcanizing agent and its interaction with the type of polydiorganosiloxane used.

20 (a) A silicone rubber base was prepared by mixing 100 parts of a hydroxyl endblocked polydimethylsiloxane with a Williams Plasticity Number of about 150, with 25 parts of a reinforcing fume silica having a surface area of 250 m<sup>2</sup>/g. The Williams Plasticity Number was determined using the procedure of ASTM—D926 with a sample weight of 4 times the specific gravity of the polydimethylsiloxane of 0.98. The base also comprised 7.5 parts of a hydroxyl endblocked

25 polydisiloxane fluid with a viscosity of about 0.042 Pa.s to prevent the base from crepe aging.

The silicone rubber base was then compounded into an uncatalyzed stock by mixing 100 parts of base with 100 parts of ground quartz with an average particle size of 5 micrometres on a 2 roll mill.

30 Portions of the uncatalyzed stock were then mixed with gamma-methacryloxypropyltrimethoxysilane in the amounts shown in Table V, based on 100 parts of base. The first two portions were catalyzed with 1.0 part of a vinyl specific organic peroxide vulcanizing agent consisting of 50 percent by weight of 2, 5-bis (tert-butylperoxy)—2, 5-dimethylhexane dispersed on an inert carrier powder. Two more portions were catalysed with 1.3 parts of a non-vinyl specific vulcanizing agent consisting of 50 percent by weight of 2, 4-dichlorobenzoylperoxide dispersed in an inert fluid. The catalyzed portions were

35 of the test were as shown in Table V.

The results show that when a vinyl specific vulcanizing agent is used with a non-vinyl containing polydiorganosiloxane, the composition does not cure. When a non-vinyl specific vulcanizing agent is used with a non-vinyl containing polydiorganosiloxane, the composition does cure. The results further show that the addition of the gamma-methacryloxypropyltrimethoxysilane in the composition with the non-

40 vinyl polymer and vinyl specific vulcanizing agent does not aid the curing process. When the non-vinyl containing polydiorganosiloxane and the non-vinyl specific vulcanizing agent are used with the gamma-methacryloxypropyltrimethoxysilane, the tensile strength is significantly improved over that obtained without the silane.

(b) The silicone rubber base described in Example 1 (A) above was compounded into an

45 uncatalyzed stock in the same manner as the base in (a) above. Portions of the uncatalyzed stock were then using the amount of silane and the two vulcanizing agents as specified in Table V. The catalyzed portions were molded into test slabs as described in Example 1 above, and then tested as described in Example 1. The results of the tests were as shown in Table V.

50 The results of these tests show that when a polydiorganosiloxane contains vinyl radicals, it can be vulcanized with either a non-vinyl specific or a vinyl specific vulcanizing agent. The results further show that in both cases the addition of gamma-methacryloxypropyltrimethoxysilane significantly improved the tensile strength over that of the samples prepared without the addition of the silane.

TABLE I

| Sample | Extending<br>Filler | Silane | Durometer | Tensile<br>Strength<br>MPa | Elongation<br>% | Tear<br>Strength<br>KN/m |
|--------|---------------------|--------|-----------|----------------------------|-----------------|--------------------------|
| A      | none                | none   | 35        | 6.37                       | 600             | 9.1                      |
| B pc   | none                | none   | 34        | 5.41                       | 540             | 13.6                     |
| C      | 100                 | none   | 59        | 3.29                       | 350             | 14.2                     |
| D pc   | 100                 | none   | 59        | 4.34                       | 240             | 15.0                     |
| E      | 100                 | 0.1    | 60        | 6.79                       | 240             | 10.7                     |
| F      | 100                 | 0.1    | 57        | 7.03                       | 200             | 9.3                      |
| G      | 100                 | 0.25   | 63        | 7.23                       | 180             | 10.9                     |
| H      | 100                 | 0.3    | 61        | 6.51                       | 200             | 8.6                      |
| I*     | 100                 | 0.5    | 62        | 6.89                       | 180             | —                        |

pc post-cured 1 hour at 250°C.

\* outside the scope of this invention.



TABLE II

| Sample  | Silane* | Amount<br>Part | Durometer | Tensile<br>Strength<br>MPa | Elongation<br>% |
|---------|---------|----------------|-----------|----------------------------|-----------------|
| J       | 1       | 0.1            | 59        | 6.48                       | 240             |
| K       | 2       | 0.1            | 59        | 5.99                       | 260             |
| L       | 3       | 0.1            | 58        | 5.17                       | 270             |
| M**     | 4       | 0.1            | 59        | 4.34                       | 300             |
| N**     | 5       | 0.2            | 59        | 3.79                       | 420             |
| Control | -       | —              | 59        | 3.29                       | 350             |

\* Silane

1. Gamma-methacryloxypropyltrimethoxysilane.
2. Gamma-methacryloxypropyl(methyl)dimethoxysilane.
3. Gamma-methacryloxypropyl(dimethyl)acetoxysilane.
4. Beta(vinylphenyl)ethyltrimethoxysilane.
5. Reaction product of chloropropyltrimethoxysilane and dimethylaminoethylmethacrylate, 50 weight percent in solvent.

\*\* For comparative purposes.

TABLE III

| Sample | Silane | Amount | Durometer | Tensile Strength MPa | Elongation % | Tear Strength KN/m |
|--------|--------|--------|-----------|----------------------|--------------|--------------------|
| O      | 1      | 0.1    | 60        | 6.79                 | 240          | 10.7               |
| P*     | 2      | 0.1    | 60        | 5.04                 | 310          | 13.1               |
| Q*     | 3      | 0.1    | 61        | 5.41                 | 260          | 13.5               |
| R*     | 4      | 0.1    | 60        | 5.07                 | 240          | 15.4               |

1. Gamma-methacryloxypropyltrimethoxysilane.

2. Vinyltriacetoxysilane.

3. Vinyltris( $\beta$ -methoxyethoxy)silane.

4. Vinyltrimethoxysilane.

\* For comparative purposes.

TABLE IV

| Sample  | Filler             | Amount<br>Of Filler<br>Parts | Amount<br>Of Silane<br>Parts | Durometer             | Tensile<br>Strength<br>MPa | Elongation<br>% |
|---------|--------------------|------------------------------|------------------------------|-----------------------|----------------------------|-----------------|
| i.      | Ground Quartz      | 100                          | 0.1                          | 62                    | 6.75                       | 200             |
| ii.     | Diatomaceous Earth | 60                           | 0.2                          | 70                    | 7.27                       | 150             |
| iii.*   | Calcium Carbonate  | 100                          | 0.1                          | 57                    | 3.93                       | 500             |
| iv.*    | Calcium Carbonate  | 100                          | 0.1                          | 55                    | 3.58                       | 470             |
| v.*     | Calcium Carbonate  | 100                          | —                            | 50                    | 3.24                       | 490             |
| vi.* pc | Calcium Carbonate  | 100                          | —                            | 53                    | 3.38                       | 490             |
| vii.*   | Clay               | 50                           | 0.1                          | 65                    | 3.82                       | 210             |
| viii.*  | Clay               | 50                           | 0.1                          | 37                    | 3.79                       | 520             |
| ix.*    | Clay               | 50                           | —                            | Did Not Cure Properly |                            |                 |
| x.* pc  | Clay               | 50                           | —                            | 25                    | 2.69                       | 750             |

pc Oven post-cured for 1 hour at 150°C

\* For comparative purposes

TABLE V

| Sample | Polymer Type | Amount Of Silane | Vulcanizing Agent  | Durometer | Tensile Strength MPa | Elongation % |
|--------|--------------|------------------|--------------------|-----------|----------------------|--------------|
| a-1    | non-vinyl    | —                | vinyl specific     |           | Did Not Cure         |              |
| a-2    | non-vinyl    | 0.1              | vinyl specific     |           | Did Not Cure         |              |
| a-4    | non-vinyl    | —                | non-vinyl specific | 41        | 3.93                 | 420          |
| a-5    | non-vinyl    | 0.1              | non-vinyl specific | 45        | 5.24                 | 270          |
| b-1    | vinyl        | —                | non-vinyl specific | 56        | 3.51                 | 350          |
| b-2    | vinyl        | 0.1              | non-vinyl specific | 59        | 6.41                 | 190          |
| D      | vinyl        | —                | vinyl specific     | 59        | 4.34                 | 240          |
| E      | vinyl        | 0.1              | vinyl specific     | 60        | 6.79                 | 240          |

## CLAIMS

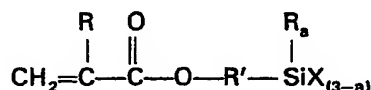
## 1. A composition comprising

(a) 100 parts by weight of silicone rubber base comprising a polydiorganosiloxane in which the organic radicals are selected from methyl, vinyl, phenyl and 3,3,3-trifluoropropyl and a reinforcing silica filler;

(b) from 25 to 300 parts by weight of a siliceous extending filler having an average particle size of less than 25 micrometres and a surface area of less than 50 m<sup>2</sup>/g;

(c) from 0.1 to 5 parts by weight of an organic peroxide vulcanizing agent capable of vulcanizing the silicone rubber base; and

(d) from 0.08 to 0.3 part by weight of an acryloxyalkylsilane of the formula



wherein each R is a hydrogen atom or a methyl radical, R' is an alkylene radical having from 1 to 4 carbon atoms, X is an alkoxy radical having from 1 to 3 carbon atoms or an acetoxy radical, and a has a value of from 0 to 2.

2. A composition as claimed in claim 1 wherein the silicone rubber base comprises 10 to 100 parts by weight of reinforcing silica per 100 parts by weight of polydiorganosiloxane.

3. A composition as claimed in claim 2 wherein the silicone rubber base comprises 15 to 75 parts by weight of reinforcing silica per 100 parts by weight of polydiorganosiloxane.

4. A composition as claimed in any of claims 1 to 3 wherein the reinforcing silica filler has a surface area of 150 to 400 m<sup>2</sup>/g.

5. A composition as claimed in any of claims 1 to 4 wherein the polydiorganosiloxane has methyl and vinyl radicals wherein the vinyl radicals are present in an amount of from 0.05 to 0.5 mole percent based on the total number of methyl and vinyl radicals.

6. A composition as claimed in any of claims 1 to 5 wherein the siliceous extending filler is present in an amount of from 25 to 200 parts by weight.

7. A composition as claimed in any of claims 1 to 6 wherein the siliceous extending filler is ground quartz, diatomaceous earth or glass.

8. A composition as claimed in claim 7 wherein the siliceous extending filler is ground quartz having an average particle size of approximately 5 micrometres.

9. A composition as claimed in any of claims 1 to 8 wherein the organic peroxide vulcanising agent is present in an amount of from 0.5 to 2.0 parts by weight.

10. A composition as claimed in any of claims 1 to 9 wherein the acryloxyalkylsilane has the formula



wherein R' is as defined in claim 1 and each X is a methoxy or acetoxy group.

11. A composition as claimed in claim 10 wherein the acryloxyalkylsilane is gamma-methacryloxypropyltrimethoxysilane.

12. A composition as claimed in any of claims 1 to 11 wherein the silicone rubber base further comprises an anti-crepe hardening agent.

13. A composition as claimed in claim 12 wherein the anti-crepe hardening agent is an hydroxyl endblocked short chain polydimethylsiloxane fluid.

14. A composition as claimed in claim 1 substantially as herein defined with reference to the Examples.

15. A method of making a composition as claimed in claim 1 which comprises mixing components (a), (b), (c) and (d) as defined in claim 1 until a homogenous mixture is obtained.

16. A process for preparing a cured silicone elastomer which comprises heating a composition as claimed in any of claims 1 to 14.

17. A process as claimed in claim 16 wherein the heating is carried out at a temperature of from 110°C to 300°C.

18. A process as claimed in claim 17 wherein the temperature is in the range of from 110°C to 175°C.

19. A secured silicone elastomer whenever prepared by a process as claimed in any of claims 16 to 18.

20. Gaskets, O-rings, diaphragms, tubing and insulating material for electrical wiring whenever made from a silicone elastomer as claimed in claim 19.

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